

[COMMUNICATION NO. 106 FROM THE RESEARCH LABORATORY OF THE EASTMAN KODAK COMPANY.]

## PHOTOMETRIC METHODS AND APPARATUS FOR THE STUDY OF COLLOIDS.<sup>1</sup>

BY S. E. SHEPPARD AND FELIX A. ELLIOTT.

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The more specific optical methods which may be applied to the study of dispersed systems are conveniently grouped under the following heads:

1. Turbidimetry, illustrated by the sulfur photometer and water turbidimeters. In this method the thickness of solution necessary to produce a given reduction in the visual resolution of some standard pattern is taken as proportional to the quantity of suspended matter.

2. Photometry of transmitted light as in the Martens photometer or the spectrophotometer.

3. Nephelometry, based on the photometric comparison of unknown and standard suspensions to determine the quantity of suspended matter.

4. Tyndallimetry, involving the photometric measurement of the intensity of the scattered light from a Tyndall cone. This method which is really an application of 2 has been very successfully applied by Werner Mecklenburg,<sup>2</sup> R. C. Tolman and his collaborators<sup>3</sup> and others.<sup>4</sup>

The method and apparatus to be described are intended to make use of any or all of the above outlined systems, as may be most desirable. In addition what is believed to be a relatively new principle in the photometry and dispersimetry of colloids is discussed and illustrated.

### Apparatus I, Horizontal Type.

This apparatus is the direct outgrowth of unpublished independent war work done in this laboratory along similar lines to the work of Tolman, *et al.*

It consists (Fig. 1) essentially of a central cell house, C (the temperature being kept constant by circulating air from an adjacent air thermostat), in which can be placed either a cylindrical, spherical or cubical cell, *c*, containing the dispersed system. Light from a central source, S, suitably collimated by lens  $L_2$ , is sent through the cell and the intensity of the light reflected at right angles by the dispersed medium is matched against another beam from the same source by means of the neutral gray wedge W. The 2 beams are brought to coincidence by the Lummer-Brodhun cube B. The comparison fields are viewed through the artificial pupil A, 1 mm. in diameter. At  $R_1$  the comparison beam is reflected either by some standard plane reflector such as magnesium carbonate or ground opal glass or from the inside of a diffusing sphere. When it is desired to measure the intensity of the transmitted light a beam of light is colli-

<sup>1</sup> Read at the St. Louis Meeting of the American Chemical Society, 1920.

<sup>2</sup> Mecklenburg, Werner, *Kolloid Z.*, **5**, 149 (1914); *Z. anorg. Chem.*, **74**, 239 (1912).

<sup>3</sup> Tolman, *THIS JOURNAL*, **41**, 296-312, 575-589 (1919).

<sup>4</sup> Smoluchowski, *Ann. Physik.*, (IV) **25**, 205 (1908); Ostwald *Kolloid. Z.* **13**, 121 (1913); Wilke u. Handovsky, *Ann. Physik.*, **13**, 1145 (1913); Onnes and Keesom, *Verlag. Akad. Wetenschappen Amsterdam*, 667, 1908.

mated at  $L_3$ , reflected at  $R_2$  and  $R_3$  from which last reflection it passes straight through the cell to the cube B. To estimate particle size by applying Rayleigh's formula for scattered radiation<sup>1</sup> it is necessary to determine the distribution of this reflected light throughout the visible spectrum. This is done with sufficient accuracy for the purpose at hand by means of the Wratten set of primary light filters. These filters are introduced conveniently at F. By making use of the split beam principle of comparison, small fluctuations of intensity of the light source are immaterial.

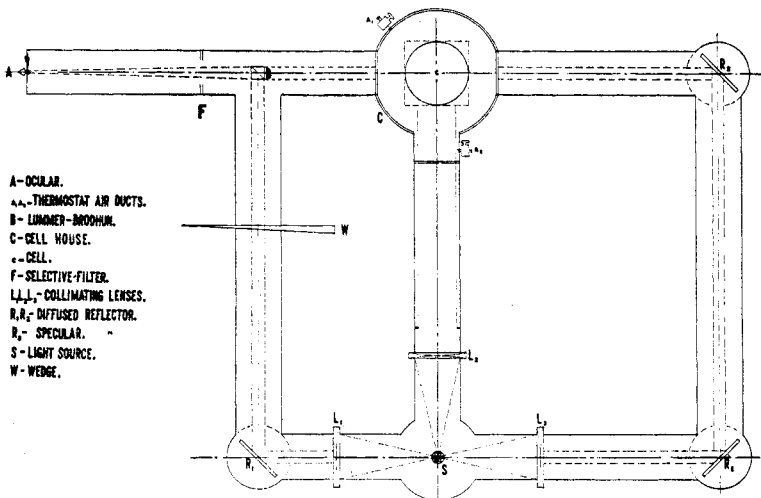


Fig. 1.

### Apparatus II, Vertical Type.

In comparison with the apparatus described above, this second type may be called the vertical plane type. The particular set-up to be described has been elaborated so that it may be used: (1) as a colorimeter, (2) as a nephelometer, (3) as a transmission and scatter photometer, (4) as a micro-photometer and (5) as a dispersimeter and dispersity comparator. The optical system of the vertical type is shown diagrammatically in Fig 2. In the photograph Fig. 3 the instrument is shown arranged to be used as a colorimeter.

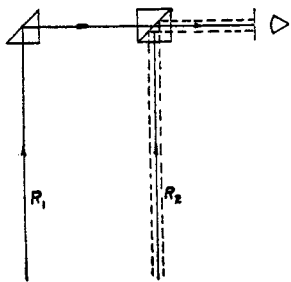


Fig. 2.

The nephelometer is easily produced by removing the colorimeter comparison cell and substituting the neutral gray wedge. The illumination train (1), Fig. 5, is used with diffused reflectors and the standard suspension is compared with the unknown as usual in nephelometry.

Fig. 4 illustrates another set-up for turbidimetry. To obtain the

<sup>1</sup> Rayleigh, *Phil. Mag.*, 12, 107-120 274-279 (1871), "Collected Papers," p. 87.

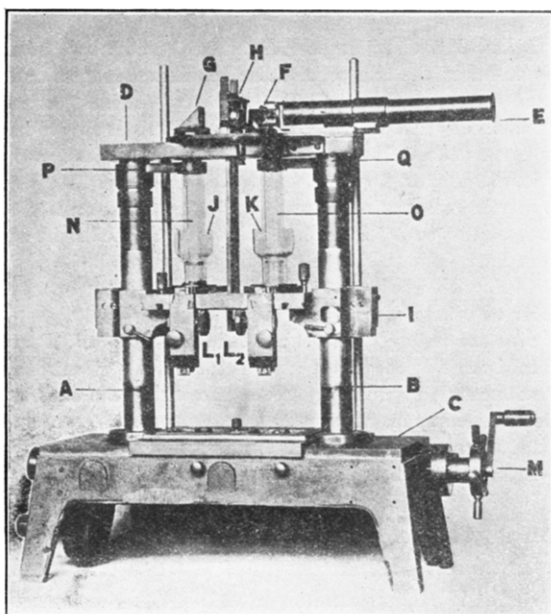


Fig. 3.

the same arrangement as in Apparatus I, *i. e.*, by photometric wedge comparison on beams from the same light source. Further, where it is desired to measure the amount of polarization in scattered light, a suitable polarizing train can be introduced.

Fig. 2. — Two parallel beams of light from the 2 objects or cells to be compared are brought into coincidence. One beam  $r_1$  is totally reflected by the prism P passing through the center field of a photometric Cube C and the artificial pupil of the telescopic eye piece T. The other beam  $r_2$  is reflected by the outer field of the photometric Cube C through T to the eye. These fields may be of a variety of shape but we have found 2 concentric

<sup>1</sup> *Loc. cit.*

lateral illumination necessary for this modification the system (1), Fig. 5, is used as in the nephelometer. In this form the instrument is in effect a Tyndallmeter or scatter photometer of similar type to that of Mecklenburg and Tolman.<sup>1</sup> For use as a transmission or opacity photometer the only change is to use system (2), Fig. 5, and remove the standard diffuse reflector from the one beam and in its place substitute another cubical cell. Transmission and scatter intensities are measured by essentially

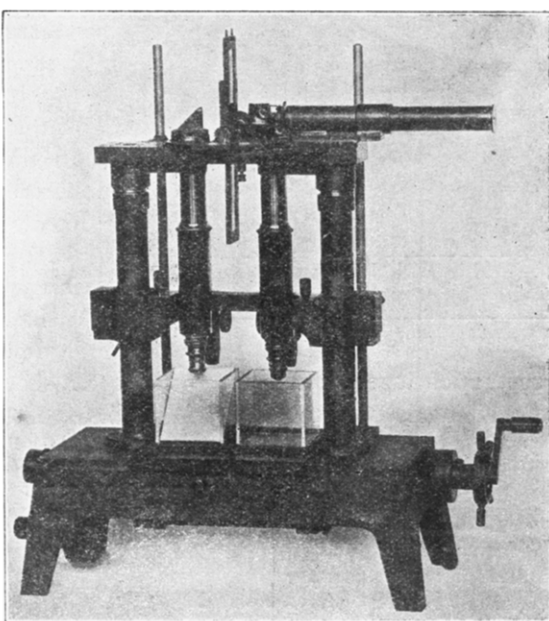


Fig. 4.

circular fields satisfactory.<sup>1</sup>

Fig. 3.—Two rigid steel uprights, A and B, perpendicular to the cast iron base, C, carry a bridge D, on which is mounted the telescope E, the Lummer-Brodhun cube F, the total reflecting prism G and the comparison cell H. A lower bridge, I, carries the usual colorimeter cells J and K, either of which may be separately raised or lowered by means of the rack and pinion movements L<sub>1</sub> and L<sub>2</sub>, or they may be simultaneously raised and lowered by means of a micrometer screw through the handwheel M. The 2 dipping tubes, N and O, are carried on rotating arms P and Q, turning on A and B, enabling them to be swung out of the way. The illumination is diffused light entering through 2 openings in the base from a simple system shown in (2) Fig. 5. The uprights A and B are provided with graduated scales as also the handwheel M. The method of operation is similar to other dipping colorimeters.

Fig. 4.—The nephelometer cups are removed and the 2 cubical cells A and B are centered with respect to the optical beams by means of a sliding metal plate pinned in correct position. This plate has 2 accurately milled pockets into which the cells are sunk. A standard diffusing reflector such as magnesium carbonate or ground pot opal glass, is used on one beam and the unknown on the other beam is matched against it by means of the neutral gray wedge, D, which is moved up and down by a rack and pinion movement.

**Dispersimeter.**—The most novel as well as the most important form of this instrument is the dispersimeter. By dispersimetry we mean measuring the *average* grain or optical heterogeneity as distinct from microscopic determinations of individual diameters and areas.

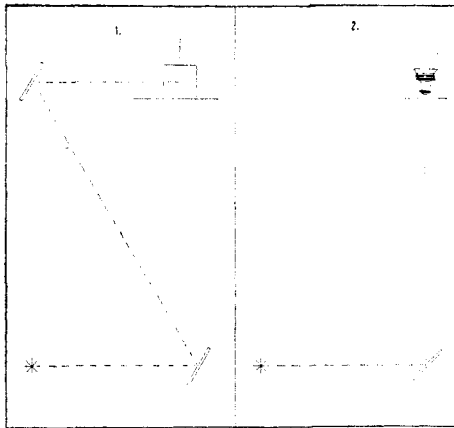
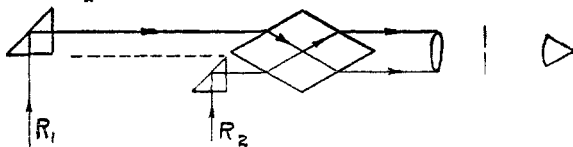


Fig. 5.

The principle was first used by one of us (S. E. Sheppard) several years ago, in a crude form, as a means of controlling the uniformity of tri-color screen plates of the Lumiere Autochrome type. In these, it may be recalled, 3 differently colored granular elements, *e. g.*, starch grains or artificial grains are mixed as uniformly as possible, and spread in a single layer on a plate. It is desirable that the "clumping" or

aggregation together of grains of one color, should not be more than a cer-

<sup>1</sup> For contrast comparison work the 2 concentric fields are most suitable but where details are to be compared this may be conveniently done by the use of an Albrecht-Hüfner rhomb as shown. This arrangement gives 2 contiguous fields whose comparison is both easy and accurate. For a recent paper on various types of photometric fields, cf. paper on "Precision of Photometric Methods," by F. K. Richtmeyer and E. C. Crittenden, *J. Opt. Soc. Am.*, 4, Sept. (1920).



tain minimum, which probability theory shows must occur. To obtain a comparison of the relative degrees of "clumping" of grains of one color, the following principle was applied. Suppose we view such a multi-colored polygrained system through a light filter only transmitting light of one of the color elements. We shall then see a number of variously sized and separated patches of that color. If we remove this to a greater distance, a point will be reached when it will be impossible to separate or resolve the color patches, and we shall have a uniform field of that color. If now we have a screen of regularly spaced, color elements of uniform size, (so-called mosaic screens, *e. g.*, hexagonal patches) and treat this similarly, if the "fusing distances" were the same, we could say that the irregular screen was equivalent to the regular screen, *i. e.*, had an equivalent periodicity or dispersity, and if the distance were *half*, that it was one half the periodicity. And this we could do for each color element, using appropriate transmission screens or filters. Evidently altering the distances of the comparison and standard screens is equivalent to altering the magnifications, and in using the principle as a microscopic method it will be sufficient to refer to corresponding magnifications.

Let 2 dispersed fields be made optically contiguous, let  $m$  and  $n$  be the respective magnifications at which they just cannot be resolved, *i. e.*, they give equally homogeneous and unresolved fields. Then as a first approximation, their dispersities are as  $m$  is to  $n$ . Now the field of magnification  $n$  can be a field of standard periodicity, *e. g.*, a half-tone grating or other standard structure so that the average dispersity of the system can be expressed as  $m/n$  per unit cross section.

Remembering that either the standard or the unknown dispersity can be magnified or reduced independently it is readily apparent that a test field of say 100X can be equated to a standard grating or graticule of 500/inch reduced to 2500/inch, which at 100X equals 2500/100 per inch as viewed. Hence the dispersity of the test is  $d = 2500/\text{inch linear}$ .<sup>1</sup>

Now it is evident that the principle here outlined for colored elements is equally valid for uncolored, black, or gray elements. It was in fact independently discovered and developed by Mr. L. A. Jones of this laboratory, for such systems (non-colored) and applied to the determination<sup>2</sup> of the granulation of photographic images. We owe to Mr. Jones' development of the principle, the more convenient method of altering the relative magnification by projection in place of the cruder method of altering the "fusion distances" alone.

The instrument shown in photograph, Fig. 6, is arranged to be used as the dispersity comparator.

Figs. 6, 7 and 8.—The bridge D, now carries 2 microscopes. These microscopes

<sup>1</sup> Commercial half-tone screens being given in lines per inch, these units are retained in the illustration; they can easily be converted to lines, etc. per cm.

<sup>2</sup> Jones and Deisch, *J. Frank. Inst.*, 190, 657 (1920).

may be independently focused by means of the usual thumb screw shown or they may be raised or lowered simultaneously by means of the micrometer screw turned at E. Above the 2 microscopes the photometer or comparison system is mounted on the baseplate B. In this set-up it is now necessary to equalize the optical paths, thus making the focal distance of the objective system the same. This is effected by moving the telescope through  $45^\circ$ , along a template, the telescope itself sliding back parallel

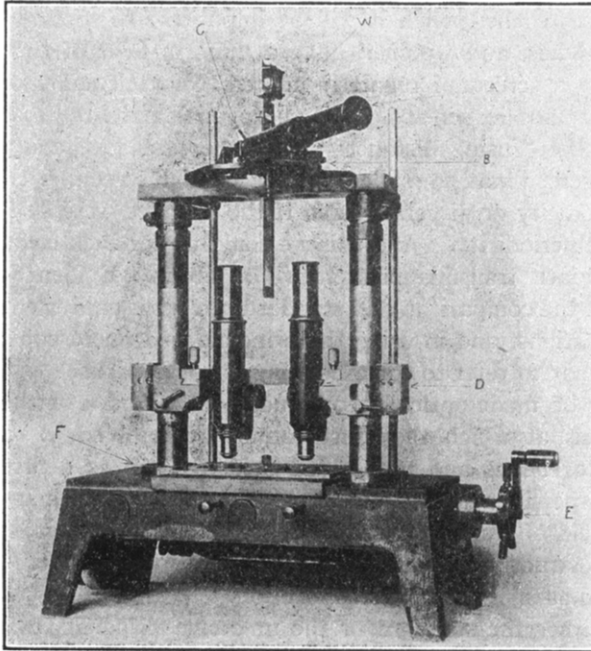


Fig. 6.

to its axis. This brings the photometric cube in position to receive the beam from a second reflection prism on the same moveable base as shown diagrammatically in Fig. 7. The photometric cube is now rotated through  $90^\circ$  and these 2 movements are all that is necessary. The 2 images whose dispersity is to be compared are projected from beneath the base of the instrument F, by means of the optical system shown in diagram Fig. 8. After the light from the source S, has been parallelized by the condenser C, it is split into 2 beams by means of the 2 deviation prisms  $P_1$  and  $P_2$ . Prisms  $P_3$  and  $P_4$  with the help of the collimating lenses  $A_1$  and  $A_2$  again make the light parallel. At this point in the optical train with the 2 rays parallel and separated by the same distance as obtains between the optical centers of the microscopes above, the 2 dispersities are introduced. D is the standard periodic structure which may be a half-tone screen or other form of grating, *e. g.*, black squares on a clear ground or clear squares on an opaque ground, depending upon the nature of the unknown dispersity X. The 2 projection lenses  $L_1$  and  $L_2$  project the images of these 2 dispersities on the focal planes of the microscope objectives above. The dispersity X as well as the standard D are mounted so that both may be moved back and forth along the optical bench by means of a rack and pinion movement. Their position relative to the lens  $L_1$ , which determines the magnification as well as their absolute positions are given by scales with verniers. The brightnesses of the 2 images are adjusted to equality by independent iris diaphragms below the focal plane.

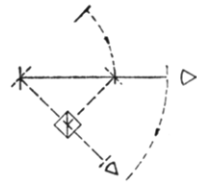


Fig. 7.

#### Limitations in Dispersity Comparisons.

These are many, but are capable of considerable reduction. (1) A very common and obvious limitation is to the case where 2 systems have the

same concentration, or space distribution. The exception is shown in Fig. 9. Here the dispersity is the same but the distribution is different. Generally, however, this factor can be taken care of. At the same time, however, we must note that with non-uniform distribution, *i. e.*, clustering of optical centers, we have already an initial lowering of dispersity.

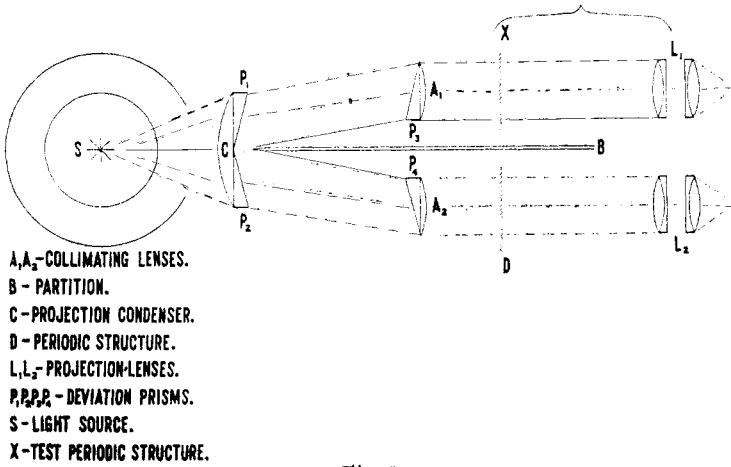


Fig. 8.

2. Dissimilarity of shape of structure elements. This is an important limitation but we believe can be practically reduced by the use of several standard dispersities or by using a system of standard deformable units.

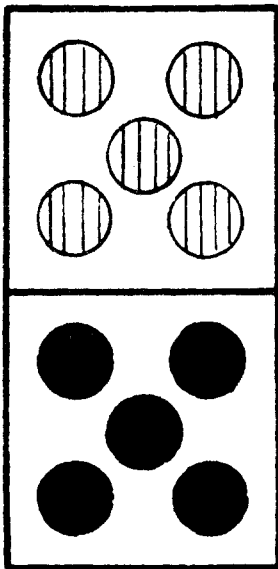


Fig. 9.

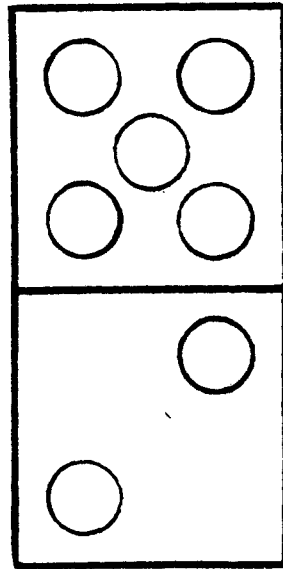


Fig. 10.

3. Differences of elementary contrast, *i. e.*, between refractive medium and the dispersed elements as illustrated in Fig. 10. This can probably be compensated for by using a graded opalescent wedge or similar system to impose a veiling glare over the more contrasty field, according to the principles worked out by Mr. L. A. Jones of this laboratory.

4. Color differences can be compensated for by selective ray filtration. In fact, it is an advantage of the present method that it makes possible now the colorimetry of dispersed vari-colored microstructures. Such a case is well illustrated when it is desired to estimate the proportion of selectively dyeing cells or elements in animal and vegetable tissues. This can readily be done by matching the test field with filtered mosaic screen plates of regular pattern and gives a new use for such plates.

5. Motion of elements. This is perhaps the most serious limitation, as affecting the field of fluid systems. It is, however, possible that this limitation may be greatly reduced and the method extended to such systems by applying uniform flow to the test material through thin cells, and flicker photometry methods to the comparison field.

In general it is to be noted that either transmitted or dark field illumination is applicable.

#### Microphotometer.

An obvious adaptation of Apparatus II as thus set up is as a microphotometer. For this, illumination train 2, Fig. 5, is employed and with the 2 microscopes in position, fitted with low power objectives incapable of resolving the elemental structure of the semi-transparent substance the unknown opacity may be compared with the wedge.

#### General Applications of Photometric and Dispersimetric Methods.

Out of a great number of obvious fields of utility we may note the following.

**I. Colorimeter.**—(1) Determination of amounts of colored substances; (2) determination of adsorption of colored substances by precipitates, gels, etc.; (3) regression of adsorption and velocity.

**II. Nephelometer.**—(1) Determination of amounts of suspensions; (2) determination of amounts of adsorption of suspended colloids; (3) measurement of the velocity of precipitation of colloids; (4) electrolyte coagulation.

**III. Turbidimeter and Scatter Photometer.**—(1) Determination of amounts of light for systems as in II.

**IV. Dispersimetry.**—(1) Dispersimetry of cell structures in tissues; (2) dispersimetry in metallurgy and ceramics; (3) study of precipitation reactions; (4) botanical and biological applications.

In conclusion we desire to express our sincere thanks to Dr. Hermann Kellner of the Bausch and Lomb Optical Company for valuable advice in designing the projection system of the dispersimeter, and our apprecia-



tion of the work of Mr. F. Reuter, formerly instrument maker to this Laboratory, who built the instrument.

### Summary.

1. We have described 2 types of photometer distinguished as vertical and horizontal types for the study of colloids.
2. The vertical plane type easily lends itself to modification for use as a nephelometer, colorimeter, microphotometer, dispersimeter and turbidimeter.
3. The horizontal type is strictly a transmission and scatter photometer of chief utility in determining particle size, comparative turbidities and coagulation velocities.

ROCHESTER, N. Y.

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[COMMUNICATION NO. 108 FROM THE RESEARCH LABORATORY OF THE EASTMAN KODAK COMPANY.]

## THE ELASTIC PROPERTIES OF GELATIN JELLIES.

BY S. E. SHEPPARD AND S. S. SWEET.

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In a previous paper there has been described a torsion dynamometer for measuring the mechanical strength of gelatin jellies.<sup>1</sup> In that paper the measure of jelly strength adopted was either the "breaking load" or the  $\frac{\text{"breaking load"} \times \text{twist}}{\text{cross section}}$ . The "breaking load" or torsional tenacity

marks the end of the stress:strain curve of the material. It is well known<sup>2</sup> that in general this value is less definitive, less immediately and certainly related to other physical and chemical properties of a material than the typical elastic constants, *viz.*, *Young's modulus* (of stretch), the *modulus of rigidity* (or shearing) and the *bulk modulus*. The torsion dynamometer described by us readily permits the determination of the *modulus of rigidity*. Calling this  $N$ , it is defined by the ratio  $N = \text{shear stress/shear strain} = g/\theta$ .

If  $\theta$  is the angle of twist in degrees,  $T$  the twisting moment in g./mm.,  $l$  the height of cylinder in mm. and  $D =$  diameter of cylinder in mm., then

$$N = \frac{583 Tl}{D^4 \theta} \text{ g./mm.}^2$$

We have found it usually desirable to calculate  $N$  in g./mm.<sup>2</sup>, as giving convenient figures.

Experimentally, this expression reduces to the following for our instrument.

<sup>1</sup> S. E. Sheppard, S. S. Sweet, and J. Scott, "The Jelly Strength of Gelatine and Glues," *J. Ind. Eng. Chem.*, 12, 1007 (1920).

<sup>2</sup> Cf. A. Morley, "Strength of Materials," Chap. 2 (Longmans Green & Co.), 1911.